

Synthesis and characterization of group 6-9 metal-rich homo- and hetero-metallaboranes

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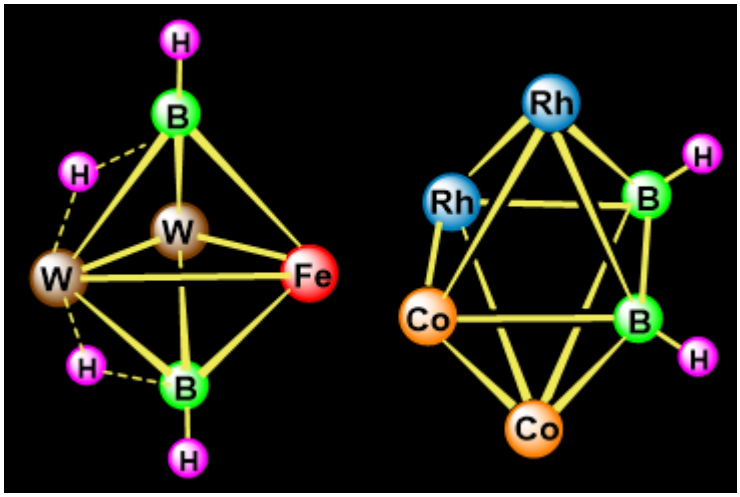
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Synthesis and characterization of group 6-9 metal-rich homo- and hetero-metallaboranes

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Abstract: To isolate the metal-rich metallaboranes of group 6-9, we have performed the reaction of various reaction intermediates, generally synthesized from the low-temperature reactions of [Cp*WCl_4] (Cp* = η^5-C_5Me_5), [(Cp*$RhCl_2)_2$], or [(Cp*$RuCl_2)_2$] and [$LiBH_4$ THF] with different transition metal carbonyl compounds. For example, the thermolytic reaction of [$Fe_2(CO)_9$] with an *in situ* generated intermediate, produced from the reaction of [Cp*WCl_4] and [$LiBH_4$·THF] afforded a trigonal bipyramidal cluster, [(μ_3-BH)$_2H_2${Cp*$W(CO)_2$}{Cp*W(CO)}{$Fe(CO)_3$}], **1** which contains a triply-bridging *bis*-{hydrido(borylene)} ligand. Similarly, the reaction of [$Co_2(CO)_8$] with *nido*-[(RhCp*)$_2(B_3H_7)$] **I** at room temperature, yielded an octahedral cluster, [(Cp*Rh)$_2B_2H_2Co_2(CO)_5$(μ_3-CO)], **2**. In this reaction, *nido*-**I** having (n+2) skeletal electron pairs (SEP) goes on for the formation of a *closo*-rhodaborane with (n+1) SEP. In addition, we have isolated a trinuclear bis(μ_3-oxo) metalla cluster [(Cp*Ru)$_3$(μ_3-$OBF_3)_2$(μ-H)], **3**. Compound **3** can be considered as cluster having trigonal bipyramidal geometry with *exo*-BF_3 fragment. All these clusters were characterized by IR, mass spectrometry, NMR, and single-crystal X-ray crystallographic analysis.

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Keywords: borylene, tungsten, metal-rich metallaborane, octahedral complex, oxoruthena cluster

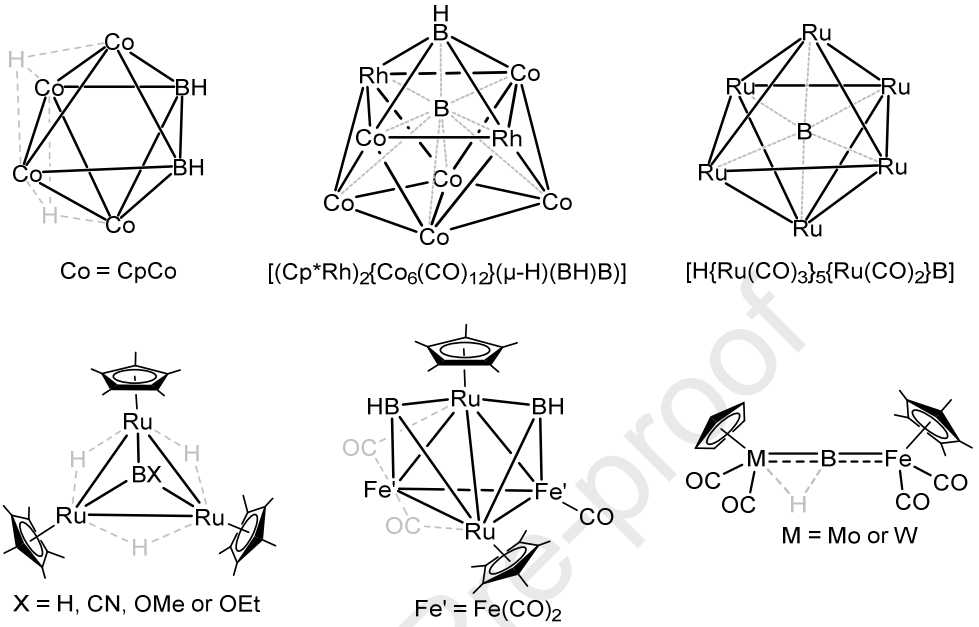
Introduction

The chemistry of metallaborane cluster has developed rapidly in the last few decades due to their diversity of fascinating structures, unique bonding and reactions.[1-3] Several approaches are there for the cluster networks expansion,[4-5] among them two major approaches are metathesis reaction with monoborane reagents[6-7] and insertion of metal carbonyl fragments into unsaturated metalla-boranes.[8] The former method is highly effective for the production of metallaborane compounds with higher vertex.[9-10] However, the latter process is more vibrant as it can act as a source of both metal carbonyl fragment or CO to form a heterometallic metallaborane clusters.[11]

Based on the metal to boron ratio, metallaborane compounds are classified into two main areas boron-rich[12-14] and metal-rich metalla-boranes.[15-16] Unfortunately, the great majority of metallaboranes in most of the synthetic methods have low metal to boron ratios. However, significant growth of metal-rich metallaboranes has been demonstrated by several reviews and articles in recent years.[17-18] Starting from borylenes, multicentred borides and higher vertex clusters, metal-rich metallaboranes have been synthesized in various structural forms. The synthesis of metal-rich metallaboranes are of specific interest owing to their several applications as super-hard materials[19] superconductors[20] and magnetic materials.[21]

In the course of our continuing interest to synthesize various metallaborane clusters, we have been exploring numerous approaches using different metal carbonyl compounds.[22] The reaction of *nido*-metallaboranes with transition metal carbonyl compounds have been found to be the most fruitful means of production of metal-rich metallaboranes.[16a,e]

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Scheme 1. Examples of some metal-rich metallaboranes.

Thus, we were interested in exploring the reactivity of $[Cp^*WCl_4]$ (Cp^* = η^5-C_5Me_5), $(Cp^*RhCl_2)_2$, and $(Cp^*RuCl_2)_2$ with borane reagents and metal carbonyl complexes such as $Fe_2(CO)_9$ and $Co_2(CO)_8$. In this report, we have described the synthesis and structure of various metal-rich metallaboranes.

Experimental

General Procedures and Instrumentation.

All the experiments were conducted under argon atmosphere using standard Schlenk line and glovebox techniques.

Purification of common Solvents (Hexane, Toluene, THF) were achieved by distillation from suitable drying agents like sodium/benzophenone under argon. C_6D_6 and $CDCl_3$ solvents were stored over activated molecular sieves. $[Cp^*WCl_4]$,[23] *nido*-$[(Cp^*Rh)_2B_3H_7]$, **I**,[24] and *nido*-$[(Cp^*Ru)_2B_3H_9]$, **II**[24] were synthesized according the method mentioned in literature.

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Chemicals such as, [$LiBH_4$ THF] (2.0 M in THF), nBuLi, Cp*H, [$Co_2(CO)_8$], and [$Fe_2(CO)_9$] were obtained from Sigma-Aldrich and used without any further purifications. Iodomethane (MeI) was obtained from Sigma-Aldrich and distilled prior to use. NMR spectra of all the compounds were recorded on Bruker FT-NMR spectrometers (400 or 500 MHz). The residual solvents protons were used as reference (δ, ppm, $CDCl_3$ – 7.26, C_6D_6 – 7.16) and a sealed tube containing [$Bu_4N(B_3H_8)$] (δ_B, -30.07 ppm,) in C_6D_6 was used as external reference in ^{11}B NMR, which was synthesized according to the method in the literature.[25] Thin-layer chromatography (TLC) was performed on 250 mm diameter aluminium-supported silica gel plates (Merck 105554 TLC silica gel 60 F_{254}). The infrared spectra (IR) were recorded on a FT/IR-4100 JASCO spectrometer in CH_2Cl_2 solvent. Electrospray mass (ESI-MS) spectra were recorded on an Agilent 6545 Q-TOF LC/MS instrument.

Synthesis of 1: In a flame-dried Schlenk tube [Cp*WCl_4] (0.1 g, 0.21 mmol) in 10 mL toluene was treated with 5-fold of [$LiBH_4$.THF] (0.7 mL) at -78 ˚C and stir for 1 h in room temperature. The residue was extracted into hexane after removal of toluene and filtered through a frit using celite. The brownish-green hexane solution was dried in vacuo and taken in 10 mL of THF. The solution is heated at 60 ˚C for 16 h in presence of [$Fe_2(CO)_9$] (0.02 g). The solvent of reaction mixture was evaporated in vacuo and the residue was extracted into hexane, then passed through celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic purification using silica gel TLC plates. Elution with a mixture of hexane:dichloromethane (90:10 v/v) produced yellow solid **1** (0.012 g, 12 %) along with known compounds [{Cp*$W(CO)_2$}$_2H_2(\mu_3$-$BH)_2${$Fe(CO)_2$}][26] (0.010 g, 10 %), [{Cp*$W(CO)_2$}$_2(\mu_3$-$BH)_2${$Fe(CO)_3$}][26] (0.020 g, 20 %), and [$(Cp^*W)_2B_5H_9$][27] (0.015 g, 20 %).

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1: MS (ESI^+): *m/z* calculated for $[C_{26}H_{34}B_2FeO_6W_2\text{-}(3H+2CO)]^+$: 829.0804, found: 829.0269. $^{11}B\{^1H\}$ NMR (128MHz, $CDCl_3$): 87.9 (s, 1B), 62.4 (s, 1B) ppm. ^1H NMR (500MHz, $CDCl_3$): 7.72 (br, 1H, BH_t), 7.54 (br, 1H, BH_t), 2.19 (s, 15H, $C_5\underline{Me}_5$), 1.97 (s, 15H, $C_5\underline{Me}_5$), -10.64 (1H, W-*H*-B), -12.44 (1H, W-*H*-B), ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 218.4 (CO), 98.7 (s, $\underline{C}_5Me_5$), 98.1 (s, $\underline{C}_5Me_5$), 11.7 (s, C_5Me_5), 10.2 (s, $C_5\underline{Me}_5$) ppm. FTIR (CH_2Cl_2): 2415 (BH_t); 2014, 1943 (CO) cm^{-1}.

Synthesis of 2: In a flame-dried Schlenk tube, *nido*-**I** (0.15 g, 0.29 mmol) in 15 mL hexane was reacted with $[Co_2(CO)_8]$ (0.198 g, 0.58 mmol) at room temperature and stir for 24 h. The residue was extracted into hexane after removal of solvent and passed through a frit using celite. The mother liquor was kept at -40 ˚C to remove $[Co_4(CO)_{12}]$ by filtration of mother liquor. After the removal of solvent from filtrate, the residue was subjected to chromatographic purification using silica gel TLC plates. Elution with a mixture of hexane:dichloromethane (80:20 v/v) in inert atmosphere produced black solid **2** (0.036 g, 16 %) along with a known compound $[(Cp^*Rh)_2(\mu\text{-}CO)(\mu_3\text{-}BH)_2\{Co(CO)_4\}]$[26] (0.044 g, 20%).

2: HRMS (ESI^+): *m/z* calculated for $[C_{26}H_{32}O_6B_2Co_2Rh_2+Na]^+$: 808.9056, found: 808.9052. $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6): 168.0 (s, 1B), 152.5 (s, 1B) ppm. ^1H NMR (500MHz, C_6D_6): 9.35 (br, 2H, $B\underline{H}_t$), 1.78 (s, 15H, $C_5\underline{Me}_5$), 1.77 (s, 15H, $C_5\underline{Me}_5$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 103.7 (s, $\underline{C}_5Me_5$), 102.0 (s, $\underline{C}_5Me_5$), 9.8 (s, $C_5\underline{Me}_5$), 9.1 (s, $C_5\underline{Me}_5$) ppm. FTIR (CH_2Cl_2): 2461 (BH_t), 1996 (CO) cm^{-1}.

Synthesis of 3: In a flame-dried Schlenk tube, *nido*-**II** (0.05 g, 0.096 mmol) was stirred with $[BF_3.OEt_2]$ (0.1 mL, 0.2 mmol) in THF at room temperature for 1 h. The volatile components were removed under vacuum. The residue was extracted into hexane:CH_2Cl_2 mixture after removal of solvent and passed through a frit using celite. The residue was

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subjected to chromatographic purification using silica gel TLC plates. Elution with a mixture of hexane:dichloromethane (40:60 v/v) in inert atmosphere yielded blue **3** (0.04 g, 46 %)

3: MS (ESI^+): *m/z* calculated for $[C_{30}H_{46}B_2O_2F_6Ru_3+Na]^+$: 902.0654, found: 902.0642. ^{19}F NMR (470 MHz, C_6D_6, 22 °C): δ = -146.16 (br, $^{10}BF_3$), -146.22 (br, $^{11}BF_3$) ppm. $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 22 ˚C): δ = 1.0 (s, 2B) ppm. ^1H NMR (500 MHz, C_6D_6, 22 °C): δ = 1.63 (s, 30H, $C_5\underline{Me}_5$), 1.62 (s, 15H, $C_5\underline{Me}_5$), -15.68 (s, 1H, Ru-H-Ru) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 22 ˚C): δ = 95.2 (s, $\underline{C}_5Me_5$), 93.4, (s, $\underline{C}_5Me_5$), 11.1 (s, $C_5\underline{Me}_5$), 11.0 (s, $C_5\underline{Me}_5$) ppm. FTIR (CH_2Cl_2): 1433, 1377 (B-O), 1266, 882 (B-F) cm^{-1}.

X-ray structure Determination.

Crystallographic information of compounds **1-3** is given below. Suitable crystals of **1, 2** and **3** were produced by slow diffusion of dichloromethane-hexane mixture. The crystal data of **1** was collected and integrated by using a D8 VENTURE Bruker AXS diffractometer at 150(2) K, **2** using Bruker axs Kappa Apex-II CCD diffractometer at 296(2) K and **3** using Bruker axs kappa Apex3 CMOS diffractometer at 299(2) K with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. The structures were solved by dual-space algorithm using SHELXT program[28] and refined with full-matrix least-squares methods based on F^2 (SHELXL program). Olex2 software used for the drawing of all the compounds.[29]

Crystal data for **1**: CCDC 2048248, $C_{26}H_{34}B_2FeO_6W_2$, Mr = 887.70, monoclinic, $P2_1/c$, a = 16.3632(19) Å, b = 9.9059(11) Å, c = 17.6686(18) Å, α = 90˚, β = 91.271(4)˚, γ = 90˚, V = 2863.2(5) $Å^3$, Z = 4, ρ_{calcd} = 2.059 mg/m^3, μ = 8.552 mm^{-1}, F(000) = 1688, R1 = 0.0359, wR2 = 0.0965, 6549 independent reflections [2θ ≤ 55.0˚] and 357 parameters.

Crystal data for **2**: CCDC 2052992, $C_{26}H_{32}B_2Co_2O_6Rh_2$, Mr = 785.81, monoclinic, $P2_1/n$, a = 11.319(5) Å, b = 15.288(7) Å, c = 16.746(7) Å, α = 90˚, β = 93.575(17)˚, γ = 90˚, V =

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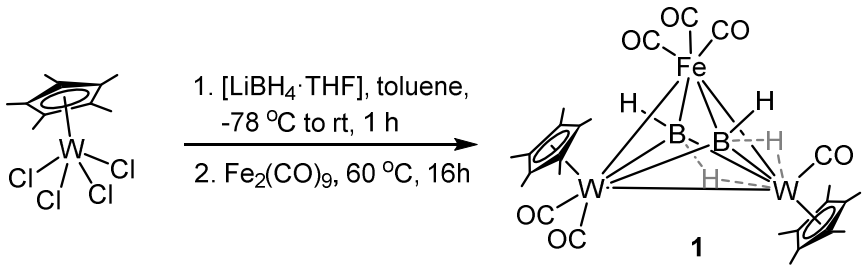
2892(2) Å^3, Z = 4, ρ_{calcd} = 1.805 mg/m^3, μ = 2.286 mm^{-1}, F(000) = 1560, R1 = 0.1152, wR2 = 0.2842, 4825 independent reflections [2θ ≤ 49.98˚] and 354 parameters.

Crystal data for **3**: CCDC 2045991, $C_{30}H_{45}B_2F_6O_2Ru_3$, Mr = 876.49, Orthorhombic, *Aba*2, a = 18.1307(11) Å, b = 34.026(2) Å, c = 21.9349(13) Å, α = 90˚, β = 90˚, γ = 90˚, V = 13532.0(14) Å^3, Z = 16, ρ_{calcd} = 1.721 mg/m^3, μ = 1.381 mm^{-1}, F(000) = 6992.908, R1 = 0.0395, wR2 = 0.0891, 11883 independent reflections [2θ ≤ 50.0˚] and 1005 parameters.

Results and discussion

*Bis-{hydrido(borylene)} cluster [(μ_3 BH)$_2$H$_2${Cp*W(CO)$_2$}{Cp*W(CO)}{Fe(CO)$_3$}] (**1**):*

As shown in Scheme 2, thermolysis of an *in situ* obtained intermediate, generated from the reaction of [Cp*WCl$_4$] and [LiBH$_4$ THF], with Fe$_2$(CO)$_9$ yielded yellow solid **1** along with the earlier reported clusters [{Cp*W(CO)$_2$}$_2$H$_2$(μ_3-BH)$_2${Fe(CO)$_2$}],[26] [{Cp*W(CO)$_2$}$_2$(μ_3-BH)$_2${Fe(CO)$_3$}],[26] and [(Cp*W)$_2$B$_5$H$_9$].[27] The ESI-Mass spectrum of **1** revealed a molecular ion peak at *m/z* 829.0269. The ^{11}B{^{1}H} NMR spectrum of compound **1** shows signals at δ = 87.9 and 62.4 ppm in 1:1 ratio, signifying two equivalent of boron atoms. The ^{1}H NMR spectrum displays two signals at δ = 2.19 and 1.97 ppm indicate two different types of Cp* ligands. Besides signals due to two B-H terminal protons, the ^{1}H NMR shows two upfield chemical shifts at δ = -10.64 and -12.44 ppm which demonstrates the existence of bridging W-*H*-B protons.



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Scheme 2. Synthesis of compound **1**.

The existence of Cp* ligands has also been confirmed by $^{13}C\{^{1}H\}$ NMR. The infrared spectra (IR) of **1** shows the stretching frequency for terminal B-H (2415 cm^{-1}) and carbonyl groups (2014, 1943 cm^{-1}).

In order to determine the solid-state structure of **1,** single-crystal X-ray analysis was performed on a suitable crystal obtained from a solution of compound **1** in CH_2Cl_2 and hexane solution at -2 °C. The X-ray structure of **1**, shown in Fig. 1. with the molecular formula as $[H_2(\mu_3\text{-}BH)_2\{Cp^*W(CO)_2\}\{Cp^*W(CO)\}\{Fe(CO)_3\}]$ signifies a trigonal bipyramid W_2FeB_2 core, in which one Fe and two W atoms occupied the equatorial positions and two boron atoms are in the axial positions. The W-W bond distance of 2.9946(4) Å is marginally longer in **1** compared to W-W bond distance of reported ditungstaboranes clusters.[26-27,30] The average W-Fe and Fe-B bond distances of **1** 2.758(9) and 2.079(7) respectively**,** are consistent with the W-Fe and Fe-B bond distances (2.77(11) and 2.04(9)) of $[\{Cp^*W(CO)_2\}_2H_2(\mu_3\text{-}BH)_2\{Fe(CO)_2\}]$[26]. Compound **1** has 6 skeleton electron pairs (SEP) count which is in accord with the *closo*-trigonal bipyramidal (tbp) geometry.[31]

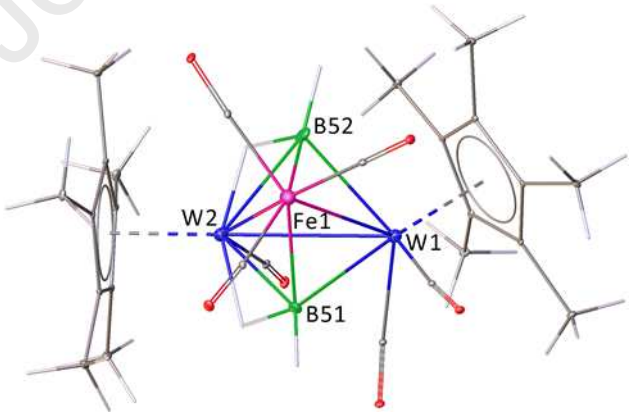


Fig. 1. Molecular structure and labelling diagram of **1**. Selected bond lengths (Å) and angles (°):W1-W2 2.9946(4), Fe1-W1 2.7592(9), Fe1-W2 2.7577(9), W2-B51

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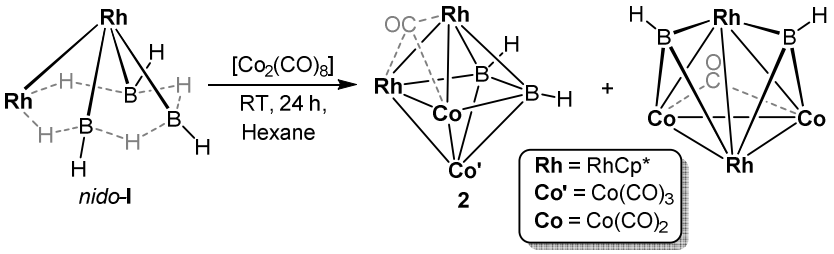
2.325(7), W2-B52 2.298(8), B51-W1 2.332(7), B52-W1 2.340(6), Fe1-B52 2.054(7), Fe1-B51 2.105(7), W1-B52-Fe1 77.5(2), W2-B51-Fe1 76.8(2).

On the basis of available literature, cluster **1** can be considered as *bis*-{hydrido(borylene)} species. Braunschweig group reported a new class of mono- and dinuclear borylene compound called hydridoborylene by intermetallic borylene transfer reaction in 2013.[32] In 2017, Tobita *et.al.* synthesized base-stabilized Hydrido (hydroborylene) tungsten complexes where W-B bond is bridged by a hydrido ligand.[33] The core geometry of **1** is analogues to that of *bis*{hydrido(borylene)} species $[H_2(\mu_3\text{-}BH)_2\{Cp^*W(CO)_2\}_2\{Fe(CO)_2\}]$ recently reported by us.[26] In cluster **1**, the W2 atom contains one CO ligand, and W1 atom contains two CO ligands. But in the case of reported *bis*-{hydrido(borylene)} species both tungsten atom comprises two CO ligands. One of the unique features of compound **1** is both the hydrido ligands are attached to one tungsten (W2) atom. Compound **1** is the rare example of transition metal borylene complex containing a triply-bridging *bis*-{hydrido(borylene)} ligand.

Reactivity of nido-$[Cp^*Rh_2(B_3H_7)]$ with $Co_2(CO)_8$:

Further to synthesized metal-rich rhodaborane we explored the reaction of *nido*-$[Cp^*Rh_2(B_3H_7)]$ (**I**) with $Co_2(CO)_8$ at room temperature that isolates black compound **2** in moderate yield. The mass spectrum of **2** shows a molecular ion peak at *m/z* 808.9052. The $^{11}B\{^1H\}$ NMR spectrum displayed two resonances at δ = 168.0 and 152.5 ppm. The ^1H NMR spectrum discloses the existence of two Cp* ligands at δ = 1.78 and 1.77 ppm and signals for B-H terminal protons at δ = 9.35 ppm.

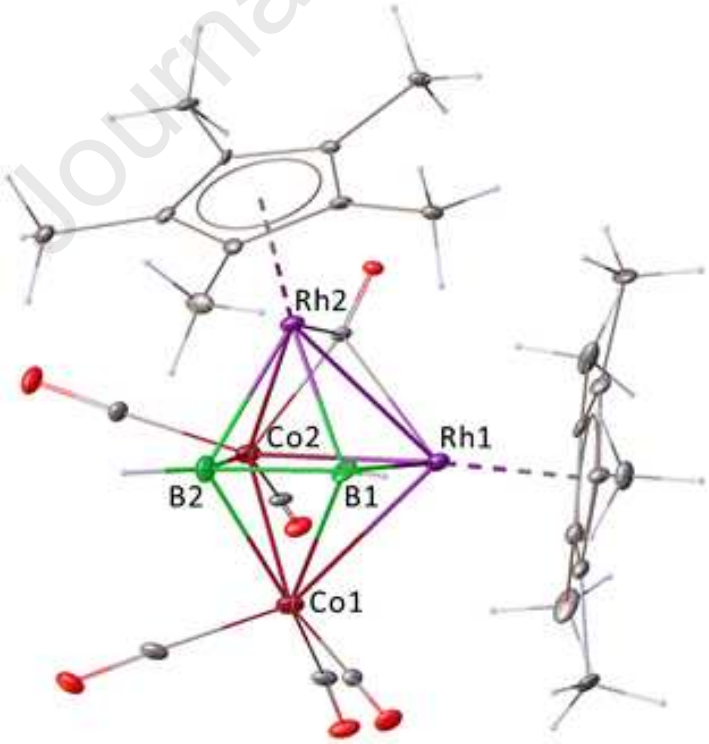
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Scheme 3. Synthesis of compound **2**.

The IR spectrum of **2** features the stretching frequency for terminal B-H (2461 cm^{-1}) and carbonyl groups (1996 cm^{-1}).

As we were unable to get exact structure from these spectroscopic data, X-ray diffraction analysis was undertaken to determine the solid-state structure on an appropriate crystal of compound **2** obtained at -2 °C. in hexane and CH_2Cl_2 solution.



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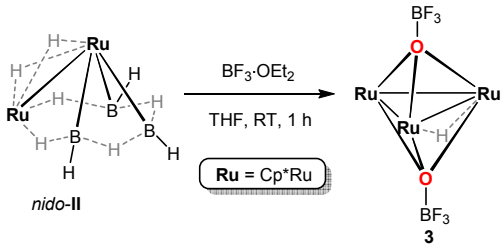
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Fig. 2. Molecular structure and labelling diagram of **2**. Selected bond lengths (Å) and angles (°): Rh1-Rh2 2.689(2), B1-B2 1.84(3), B1-Rh1 2.07(2), B1-Co1 2.07(2), B1-Rh2 2.08(2), B1-H1 1.1000, B2-Co1 2.03(2), B2-Co2 2.08(2), B2-Rh2 2.11(3); B2-B1-Rh1 103.7(12), B1-B2-Co2 95.6(13), B2-Co2-Rh1 83.1(7), B1-Rh1-Co2 77.6(6), Co1-B1-Rh2 116.0(10), Co1-B2-Rh2 116.3(12), Co1-Rh1-Rh2 82.50(8).

The crystal structure of **2**, shown in Fig. 2. signifies an octahedral geometry consisting $Rh_2Co_2B_2$, in which one rhodium atom, Rh1, two boron atoms, B1 and B2 and one cobalt atom Co2, represents the equatorial plane and while Rh2 and Co1 atoms occupy the apical position. One carbonyl capping the triangular Rh-Co-Rh face. The Rh-Rh and Rh-B bond distances in compound **2** are consistent compared to Rh-Rh and Rh-B bond distances reported rhodaboranes.[9b,16a,22a,26] *Nido*-**I** having (n+2) SEP goes on for the formation of a *closo*-rhodaborane with (n+1) SEP.[31] Compound **2** has 7 skeleton electron pairs (SEP) count which is in accord with the *closo*-octahedral geometry. Compound **2** is interesting. It's a nice skeletal isomer of *closo*-M_4E_2 clusters discussed in the past (M= Ru or Os, E= CR or Bi).[34]

*Synthesis of oxoruthena cluster **3**:*

In an attempt to isolate metal-rich ruthenaboranes, we carried out the reaction of *nido*-$[B_3H_9(Cp^*Ru)_2]$ (**II**) with mono-borane reagent $[BH_3{\cdot}THF]$ at 60 °C in THF for 15 h. This leads to the formation of known cluster *nido*-$[1,2\text{-}(Cp^*Ru)_2B_4H_9(\mu\text{-}H)]$.[24] Besides, we have isolated a blue compound **3** in 46% yield.



Scheme 4: Synthesis of compound **3**.

This compound has been characterized by IR spectroscopy, Mass spectrometry, multi-nuclear NMR spectroscopy, and single-crystal X-ray diffraction analyses. Compound **3** exhibits a sharp peak at δ = 1.0 ppm in $^{11}B\{^1H\}$ NMR spectrum. The ^1H NMR

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indicates the presence of two types of Cp* ligands in 1:2 ratio at δ = 1.62 and 1.63 ppm respectively and an upfield resonance at δ = −15.68 ppm due to the presence of Ru-H-Ru. Further the $^{13}C\{^{1}H\}$ NMR spectrum of **3** confirms the existence of two types of Cp* ligands. Based upon the spectroscopic data, we can't conclude the structure. The structure of **3** became clear from the single crystal x-ray diffraction which determined as a trinuclear bis-(μ_3-oxo) ruthena cluster [$(Cp^*Ru)_3(\mu_3$-$OBF_3)_2(\mu$-H)].

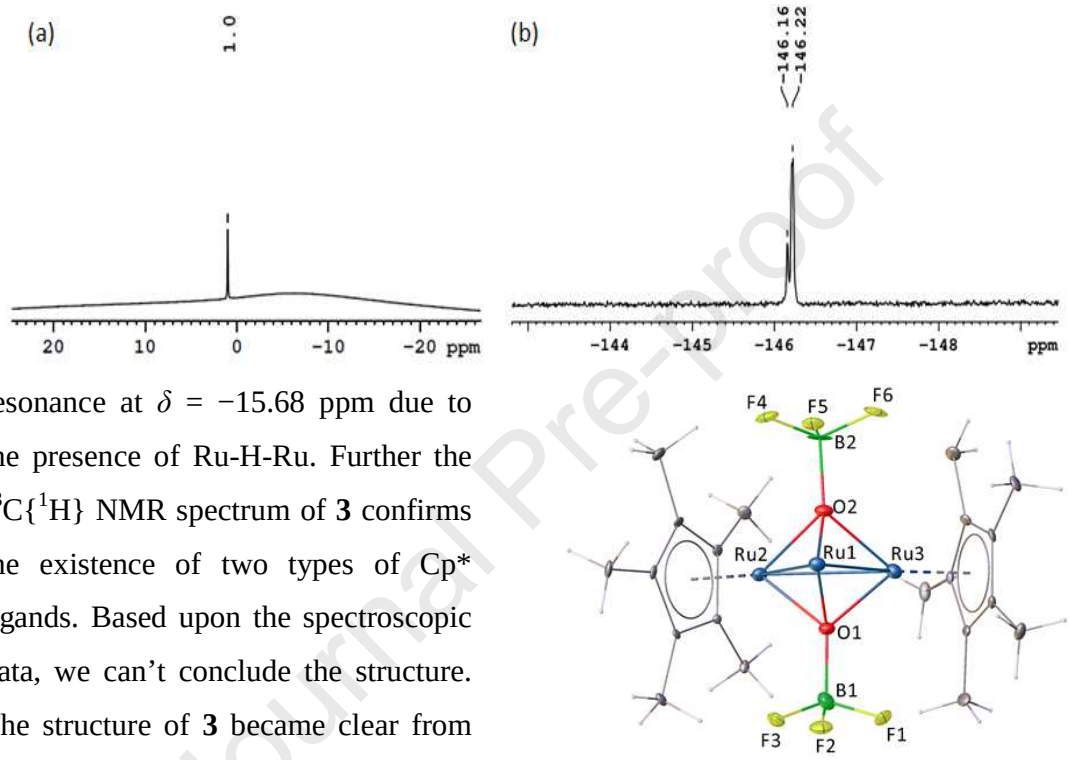


Fig. 3. Molecular structure and labelling diagram of **3** (One of the Cp* ligand attached to Ru1 is omitted for clarity). Selected bond lengths (Å) and angles (°): Ru1-Ru2 2.834(2), Ru1-Ru3 2.837(17), Ru2-Ru3 2.822(2), Ru1-O1 2.024(9), Ru2-O2 2.079(10), Ru3-O2 2.034(10), O1-B1 1.531(12), O2-B2 1.514(14), Ru1-Ru2-Ru3 60.22(5), Ru3-O2-Ru1 88.3(5).

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The core structure of **3** is similar to that of $[(Cp^*Ru)_3(\mu_3\text{-}O)_2(\mu\text{-}H)]$[35] and $[(CpRu)_3(\mu_3\text{-}O)_2(\mu\text{-}Cl)]$.[36] As shown in Fig. **3**, each oxygen atom is connected to three Ru metals and one BF_3 fragment. The molecule has a mirror plane passing through Ru3, O1, O2, B1, B2 and center of Ru1−Ru2 bond. Compound **3** can be considered as cluster having trigonal bipyramidal geometry with *exo*-BF_3 fragment. The total electron count (TEC) of compound **3** is 48 and SEP count is 6. To find out the source of O-BF_3 fragment, we explore the reaction of *nido*-$[(Cp^*Ru)_2B_3H_9]$ with $BF_3{\cdot}OEt_2$. After adding $BF_3{\cdot}OEt_2$ to *nido*-$[(Cp^*Ru)_2B_3H_9]$ in THF, the reaction mixture was stirred for 1 h at room temperature.

Fig. 4. (a) $^{11}B\{^1H\}$ NMR spectrum (b) ^{19}F NMR spectrum of **3** in C_6D_6.

A visible color change from orange to dark brown solution was observed upon the formation of **3**. The ^{19}F NMR spectrum shows two resonances, one at δ = −146.16 ppm for the coupling with ^{10}B nuclei and another resonance at δ = −146.22 ppm due to the coupling with ^{11}B nuclei ($J(^{11}B\text{-}^{19}F)$ = 6.2 Hz) (Fig. 4).[37] The mass spectrometric analysis shows a molecular ion peak at *m/z* 902.0642 which corresponds to the molecular formula $[C_{30}H_{46}B_2O_2F_6Ru_3{+}Na]^+$. The infrared spectrum indicates the presence of B-O stretching frequencies at 1377, 1433 cm^{-1}. The average B−O bond distance of 1.522 Å is comparable to the reported metallaoxaborane clusters.[38] The average Ru−Ru bond distance (2.831 Å) of **3** is slightly longer than $[(Cp^*Ru)_3(\mu_3\text{-}O)_2(\mu\text{-}H)]$[36] (2.7135(10) Å). In compound **3** the average Ru−O distances of 2.045 Å and 2.050 Å for Ru−O1 and Ru−O2 respectively are significantly longer than the bis(μ_3-oxo) complex $[(Cp^*Ru)_3(\mu_3\text{-}O)_2(\mu\text{-}H)]$ (2.004(6) Å). These bond length values lie within the range of metal-oxygen bond in reported bis(μ_3-oxo) complexes of transition metals.

Conclusions

In this article, we have described the synthesis and characterization of

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several metal-rich metallaboranes based on the reaction of cyclopentadienyl metal chlorides with boranes and metal carbonyls. Compound **1** represents one of the rare examples of transition metal borylene cluster containing a triply-bridging *bis*-{hydrido(borylene)} ligand. An *closo*-octahedral rhodaborane was synthesized from the reaction of *nido*-**I** with $Co_2(CO)_8$. Also, a trinuclear bis(μ_3-oxo) metalla cluster having trigonal bipyramidal geometry with *exo*-BF_3 fragment was synthesized. All the synthesized clusters obey Wade-Mingos rule of the polyhedral skeleton electron count and are unique considering their cluster geometries.[31]

Conflict of interest

The authors declare no conflict of interest.

Acknowledgments

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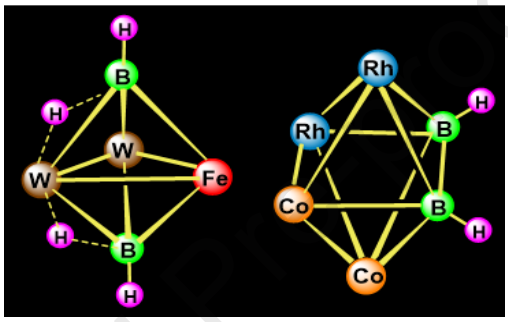
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Synthesis and characterization of group 6-9 metal-rich homo- and hetero-metallaboranes

Ranjit Bag, Suman Gomosta, Alaka Nanda Pradhan, Thierry Roisnel and Sundargopal Ghosh*



Metal rich metallaborane clusters with trigonal bipyramidal and octahedral geometry (see picture)

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- Synthesis of metal-rich metallaboranes
- Rare examples of *bis*-{hydrido(borylene)
- trigonal bipyramidal and octahedral geometry
- oxoruthena cluster

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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